## Coal Combustion By-Products in Mine Backfill: Evaluation of Water Quality at Pennsylvania Sites

Carol R. Cardone and Ann G. Kim Physical Scientist U.S. Department of Energy National Energy Technology Laboratory Pittsburgh PA, 15236

#### Abstract

Mining companies in Pennsylvania, are permitted to place coal combustion by-products in active surface mines as part of their reclamation plan. They are required to submit water quality monitoring data to the Pennsylvania Department of Environmental Protection. The National Energy Technology Laboratory of the U.S. Department of Energy copied data submitted prior to the year 2000. The resultant database includes information from 37 mine operators and 57 generator companies from the eastern United States. The water data included values of cation concentrations, pH, and acidity and alkalinity for up and down gradient samples. Because the distribution of values was not normal, a scatterscore evaluation method was developed comparing the differences between an up gradient and down gradient range of values and medians for all water quality parameters. Depending on whether down gradient values were lower or higher than the up gradient values, a score for each parameter, when plotted on a scattergram, would fall into one of four quadrants. Counting the number of values in each quadrant, multiplying by an appropriate weight and normalizing the final value produced a score that can be used to evaluate overall changes in water quality at mine sites where coal combustion by-products were placed. This method could also be used to evaluate water quality before and after placement of the coal combustion by-products and could be adapted to compare individual elements. Based on this approach, the data from the Pennsylvania Department of Environmental Protection indicated no impairment or adverse changes in water quality at the mine sites where coal combustion byproducts were placed as a backfill.

#### Introduction

According to the American Coal Ash Association<sup>1</sup> (ACAA), in 1998 more than 107 million tons of coal combustion by-products (CCB) were produced in the United States by coal burning electric utility companies. However, less than 30 percent of the CCB was used, and most of that was primarily in concrete. The remaining 70 percent are disposed of in landfills or ponds. For the past decade, the quantity of CCB disposed of in this manner has consistently increased, and with current air pollution regulations, it is expected to continue to grow unless new and beneficial uses for CCB are developed and implemented. The U.S. Department of Energy (DOE) encourages the increased utilization of CCB.<sup>2,3</sup>

Beneficial use, as an alternative to disposal includes: structural fill, soil amendments, and use in reclamation of abandoned or active surface coal mines. Points considered in the evaluation of the beneficial use of CCB at mine sites include the likelihood that the alkaline material will reduce the amount of acid produced and the possibility that trace elements contained in the CCB may leach into surface or ground water.

On April 25, 2000, The Environmental Protection Agency (EPA) issued a regulatory determination for fossil fuel combustion wastes generated as co-managed wastes.<sup>4</sup> Earlier in the year, under pressure from environmental groups, they had proposed to regulate fossil fuel wastes as a tailored Subtitle C (hazardous) material, specifically when used in mine backfill. The Department of Energy, the Office of Surface Mining (OSM) and others argued that any classification of CCB as hazardous would significantly curtail all beneficial uses of this material and that there was no evidence that CCB caused damage to health or the environment.

In their regulatory determination,<sup>5</sup>, the EPA stated that fossil fuel wastes do not warrant regulation under Subtitle C of RCRA and retained the hazardous waste exemption under RCRA Section 3001 (b) (3) (C). However, they also proposed that national regulations under Subtitle D of RCRA are warranted for coal combustion wastes when they are disposed in landfills or surface impoundments, and that such regulations and/or possibly modifications to existing regulations established under authority of the Surface Mining Control and Reclamation Act (SMCRA) are warranted when these wastes are used to fill surface or underground mines. So that coal combustion wastes are consistently regulated across all waste management scenarios, these national regulations for disposal in surface impoundments and landfills and mine filling will be applied to large volume coal combustion wastes that had been exempted under the 1993 regulatory determination. Although the EPA is concerned about placement directly into groundwater, they have not yet identified a case where placement of coal wastes can be determined to have caused damage to groundwater. When mine filling is conducted properly and there is adequate oversight of the remediation activities, EPA generally encourages the practice of remediating mine lands with coal combustion materials. Although no case of environmental damage due to this practice has been identified, it has generally been difficult to evaluate water quality changes at mine sites.

### Data

The Environmental Science and Technology division of the U.S. Department of Energy's National Energy Technology Laboratory (NETL) has a research program on CCB that includes monitoring water quality at several mine sites reclaimed with CCB.

In 1993, while contacting several states about their CCB policies, it became apparent that the Pennsylvania Department of Environmental Protection (PADEP) had the most extensive data on the use of CCB in mine reclamation. The PADEP requires mining companies that place CCB in surface mines apply for a modification of their mining permit (Module 25 and Module 25A) and submit quarterly and annual reports. DOE personnel have been allowed to copy the Module 25 applications and the submitted monitoring reports at five PADEP offices.

The information from 37 operators included name and location, the number of acres in the mining permit and the number proposed for placement of CCB, information on the ash generator, and the volume of ash to be placed daily, monthly or annually. The water quality data included the analysis of water samples from 593 monitoring points, such as wells, springs, pools, ponds, pits, and discharges. In addition to data on the sampling point, flow, temperature, alkalinity and/or acidity, pH, and the concentrations of iron, manganese, aluminum, sulfate, total dissolved solids and total suspended solids were measured. The concentrations of trace metals were included in annual reports.

The water quality, ash composition and leachate data were transcribed into spreadsheets. There are over 6,300 rows in the water quality data set; sampling locations were identified structurally as above (up gradient) or structurally below (down gradient) the ash placement sites. The period for the water monitoring data extended from 1978 to 2000.

To evaluate the effect that the use of CCB in mine reclamation has on water quality requires merging water data that has been submitted to the PADEP in quarterly and annual reports. Between the 2 reports, there are 35 water quality parameters. The number of parameters makes comprehensive evaluation of the effect of CCB placement on water quality difficult. The mine water system is a complex chemical system that involves inputs from meteoritic water and ground water, and chemical reactions between pyrite, spoil, overburden, and the CCB. The volume of water in the system, the rate of infiltration and evaporation, and the type of sampling points are also independent variables. Even tracking a few major parameters, such as pH, Fe, Al, and Mn, produces a complex data set that is not easy to evaluate.

In addition to the number of variables, there were other difficulties in trying to analyze the PADEP data. At several sites, it was not clear whether missing data indicated a value below the analytical detection limit or no analysis. Also, the date CCB were placed was not available for some sites, or could only be estimated as some point within a given year. The amount of ash and the placement schedule were generally not available. In many cases, it was difficult to match up gradient and down gradient sampling points, and limiting the number of variables evaluated required a qualitative decision on the importance of each water quality parameter.

The annual reports did not include flow rates or volume data. Concentrations are a function of both the chemical reaction rate and the amount of water in the system. The amount of water is related to flow from other groundwater sources, and to the amount of precipitation and the rate of infiltration. Since there are no data on the volume of water or on flow into or out of the system, the concentration values cannot be normalized to an objective standard.

Based on previous evaluations of the data,<sup>6, 7</sup> the distribution of data values cannot be assumed to be normal. Therefore, statistical tests of significance that apply to normally distributed data sets, e.g., t-test, should not be used to compare the water quality data. Also, the data sets are relatively small, sometimes fewer than 10 values. Therefore, the central limit theorem (the sample mean equals the population mean when n is large) does not necessarily apply.

For each sampling point, the data set may consist of up to 35 variables obtained at a given point in time. The values, other than pH, are concentrations in mg/L. If there is a relationship between variables, it is most likely a function of the geologic conditions and would vary for each site. Changes in the values of each variable are related to additions to the system, removals from the system, and changes in the volume of water in the system. Variability is normal in water quality parameters, because of precipitation, snow melt, groundwater discharge and recharge, and possible changes in the flow path. In this case, data on the volume of water or flow rate are not known.

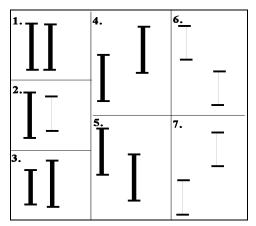
While comparing the different ways to evaluate changes in water quality sites, a concern was that the association between up and down gradient sampling points was not always certain. There are a number of ways to analyze water quality data such as: Piper Plot, Stiff Diagram, Schoeller Diagram, Durov method, Langlier-Ludwig method, and radial diagrams. Most of these methods had limitations and were not appropriate ways to look at this data set. For example, the Piper Plot and Stiff Diagram<sup>8</sup> only include major elements, and because they are visual comparisons, and not a mathematical evaluation, they are not easy to interpret.

### **Method - Scatterscore**

A less rigorous but more practical approach is to develop a single mathematical score that compares all values in one data set versus all values in another data set. At each site there is at least one up gradient sampling point and one down gradient sampling point. Values based on differences between parameters at up and down gradient sampling points were plotted on a scattergram and a scatterscore<sup>9</sup> was calculated. This approach was also applied to water samples obtained at the down gradient sites for before and after placement of CCB. Because water quality parameters are essentially different in surface and underground environments, comparisons are considered valid only between samples from similar sources, i.e., stream samples should not be compared to well samples.

### Range Comparison

At each sampling point all values, for each parameter, fall within a range with maximum and minimum values. When compared, if treatment has a positive effect, the range of the down values will be equal to or lower that the range of the up values. There are seven possible relationships between ranges defined by high or low values at the up and down sampling points (Fig.1). The Up range is on the right and the Down range is on the left. The top bar represents the maximum value and the lower bar the minimum value.



**Figure 1**. Relationship between up and down gradient ranges.

The up range  $(R_U)$  is equal to the maximum parameter value measured at the up gradient sampling point minus the minimum parameter value for the same sampling point. The down range  $(R_D)$  is the same for the down gradient sampling point.

$$R = (Max - Min)$$
  $R = (Max - Min)$ 

The range total  $(R_t)$  is equal to maximum up or down minus minimum up or down. The sum of the ranges  $(\Sigma R)$  then is equal to the sum of the difference between the maximum and minimum values for up and down ranges. The range value  $(R_v)$  equals the range total divided by the sum of the ranges. This measures the degree of overlap between the ranges.

The difference,  $\Delta$ Max, between the maximum value of the up set and the maximum down set would be positive if the maximum up is greater and negative if the maximum up is less than maximum down. Dividing  $\Delta$ Max by its absolute value yields values of 1 or -1.

$$\Delta Max = Max_U - Max_D$$

$$\Delta Max_{abs} = \frac{\Delta Max}{ABS(\Delta Max)}$$

Combining these factors produces the range comparison (RC)

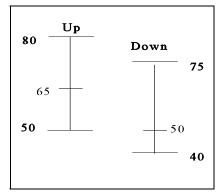
$$RC=R *\Delta MAX$$

For example, in Figure 2, if all the up values are between 80 and 50 and the down values are between 75 and 40, the range total for all values would be 80 minus 40. It does not matter which set is higher or lower.

Defined Ranges based on Fig 2.

$$\Delta Max_{abs} = \frac{\Delta Max}{ABS(\Delta Max)} \quad (\frac{5}{5} = +1)$$

$$RC = R_v * \Delta MAX_{abs} \quad (.53 * 1 = .53)$$



**Figure 2**. Example of range comparison.

Table 1. Possible Values of Range Parameters

Type <sup>1</sup>	$R_{t}:\Sigma R$	R	ΔMax	RC	
I	2	.5	0	0	
II	$R_{\rm t} < \Sigma R$	<1	+1	<0,1>	
III	$R_{\rm t} < \Sigma R$	<1	-1	<0,-1>	
IV	$R_{\rm t} < \Sigma R$	<1	-1	<0,-1>	
V	$R_{\rm t} < \Sigma R$	<1	+1	<0,1>	
VI	$R_{t} > \Sigma R$	>1	+1	>1	
VII	$R_{t} > \Sigma R$	>1	-1	<-1	

<sup>&</sup>lt;sup>1</sup> Type refers to figure 1.

Table 1 summarizes the possible relationships between the up and down ranges. Based on those factors, the RC can have values of greater than 0 or less than 0. If the down range is lower, the RC will be between 0 and 1. If there is no overlap in the up and down ranges, the RC will be greater than 1 if the down range of values is lower.

### Median Ratio

The range comparison does not completely describe the data set. Therefore, in addition to the ranges, the medians were evaluated. Since the data was not normally distributed, the median is the appropriate statistical descriptor for this type of data, and a ratio of up and down medians was included.

The median ratio (MR) is the up median divided by the down median and can have values in 2 ranges, between 0 and 1 or greater than 1. The MR is greater than 1 if the median for the up values is larger than that of the down values. A value between 0 and 1 indicated the median of the down values is greater. A value of 1 indicates the medians are equal. In the example of figure 2, the up median (65) is greater and the value of MR is greater than 1.

$$MR = \frac{Med_U}{} = \frac{65}{} = 1.3$$

### Scatterscore

The values of RC and MR are calculated for all variables in the data set. Using these values, a point for each parameter in a data set will be placed in one quadrant of a scattergram (Fig. 3). Each quadrant will represent improvement, mixed results or no improvement. A weight is assigned to each quadrant. Table 2 shows values of RC and MR with quadrant weights. Quadrant 1 has an assigned weight of 0.50. Points in quadrant one indicate that there was improvement in the range but not in the median. Quadrant 2 is assigned a weight of 0.75 and indicates that there is improvement in both the range and the median. Quadrant 3's assigned weight is 0.25 and in this quadrant there is no improvement in the median or range. Quadrant 4 was assigned 0.50 because there is improvement in the median but not in the range.



**Figure 3**. Scattergram defined by values of RC &MR.

Table 2. Quadrant Values for Scattergram

Quadrant	RC	MR	Weight
1	>0	<0,1>	0.50
2	>0	>1	0.75
3	<0	<0,1>	0.25
4	<0	>1	0.50

Counting the number of points in each quadrant and multiplying them by the appropriate weight produces a scatterscore (SS), a number that is a semi-quantitative evaluation of changes at a site. In this data set, there are 35 variables and if all variables improved the highest possible score would be 27. If there was no improvement, the score would be 9. Missing data would affect the score; therefore, the scatterscore is normalized. N represents the number of variables available in a data set.

$$SS = SS_N$$

Scores ( $SS_N$ ) above 18 are indicative of improved water quality. A score below 12 could indicate a possible problem. If the score was between 13 and 18, mixed results are indicated. At least 2 scatterscores would normally be calculated for each site, one for up and down and one for before and after, at a sampling point. In many cases, more comparisons could be made, depending on the number of sampling points. Table 3 shows the 20 mine sites with the number of up and down comparisons and also the before and after comparisons. The first column indicates the site number followed by the up and down  $SS_N$  values for those sites. Site number 1 has 2 up (U) and 3 down (D) comparisons with 3 down before (Db) and after (Da) CCB comparisons. Independent of the number of comparisons, an average score was calculated for each site. Figure 4 shows the average scores for 20 mine sites where CCB were placed. The highest score was 23.6 and the lowest was 13.9 with an average score of 18.3. In the mine sites evaluated in this paper, 40% had average scatterscores above 18, and another 60% had scores between 13 and 18. There were no sites with values less than 12.

Table 3. Normalized scatter scores for all comparisons.

Site Number					D1bvsD1a	D2bvsD2a	U1vsD3	U2vsD3	D3bvsD3a	Average SS
1	19.9	13.0	17.5	14.1	13.3	16.7	12.8	11.4	17.3	16.2
2	23.6	17.4	19.8	19.7	18.4	18.0	20.8	22.8	14.2	20.1
3	18.3		23.7		19.3	20.5				20.4
4	18.7	17.3	20.5	17.7	13.3	20.2	22.1	23.5	13.5	19.2
5	13.9	13.5			19.2					16.2
6	20.9				20.3					20.6
7	22.5				16.0					19.3
8	23.3		20.3			18.6	20.0			20.6
9	16.1				22.0					19.1
10	18.0				17.1					17.5
11	17.4				13.7					15.5
12	16.6		12.3							14.4
13	15.4				13.5					14.4
14	16.5		21.5		14.7	17.5	18.0			17.6
15	19.3				13.7					16.5
16	15.2		16.7		15.6		15.4			15.7
17	22.2				12.4					17.3
18	14.0				19.8					16.9
19	15.8				16.0					15.9
20	18.5				18.4					18.5

The scatterscore method can also be applied to evaluations of individual elements. For example, the range comparison and median ratio values for arsenic (As) and cadmium (Cd) (Fig.5) were extracted from the site files and a point was placed in the appropriate quadrant. For a given site, there was a possibility of 9 comparisons. Therefore, the sum of the number of points in a quadrant times the weight were multiplied by 9 and divided by the total number of actual comparisons. The maximum possible value was 6.75 and the minimum value was 2.25. The highest and lowest score for As was 6.75 and 3.6 respectively with an average value of 5.31. The highest and lowest for Cd was 6.75 and 2.25 respectively with an average value of 4.85. Values at or above 4.5 would be considered as improvement, and values below 3.00 would indicate no improvement. Values between 3.25 and 4.25 would indicate mixed results. The scatterscore results for As and Cd were as follows: As, had 94% of the sites at 4.5 or above and only 1 site was in the mixed results category (3.6). No values for As equaled the lowest value of 2.25. Cadmium values were 73% for 4.5 and above and 27% below 4.5. Cadmium had one value of 2.25. A value such as this would fall in quadrant 3 and indicate that the actual data should be reviewed. In figure 5, the missing bars indicate no data in the file.

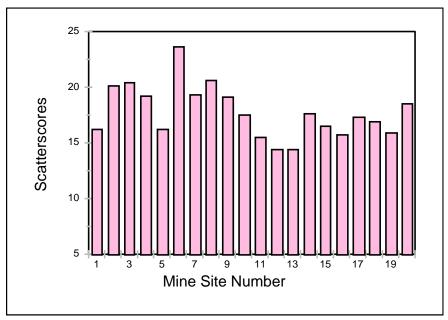
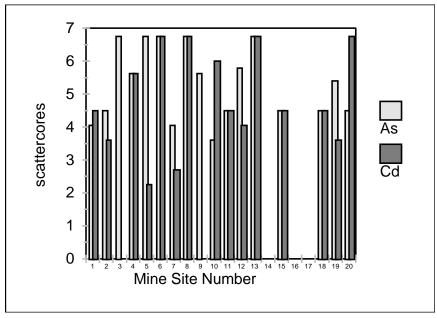


Figure 4. Scatterscore values of 20 Mine Sites.



**Figure 5.** Scatterscore values for As and Cd Concentrations at Mine Sites.

# Summary

The scatterscore is a very general indicator of changes in water quality. It is based on all the available data, but does not include any qualitative evaluation of site characteristics or the adequacy of the data set. Specifically, it does not place greater emphasis on any one parameter or set of parameters. It is simply an attempt to base an evaluation on all parameters over a variable period of time.

A more accurate evaluation of changes in water quality might focus on key parameters or monitor changes at a sampling point over time, if changes in flow or volume could be factored into the evaluation. As given, the data for these sites is not easily treated with such an approach. Therefore, a reconnaissance method, such as the scatterscore, can be used to track general changes and to serve as an indication that a more through evaluation is necessary. Using this method, the scatterscores indicated definite water improvement in over 40% of the evaluated sites. Based on this approach, the data from the PADEP indicated no adverse changes in water quality at the mine sites where coal combustion by-products were placed as a backfill.

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